УДК 535.37

N. A. Shekhovtsov[1, 2], K. A. Vinogradova[1, 2], A. S. Berezin[2], T. S. Sukhikh[1, 2], V. P. Krivopalov[3], E. B. Nikolaenkova[3], M. B. Bushuev[1, 2]

[1]Novosibirsk State University, 630090, Russia, Novosibirsk, Pirogova St., 2, shna1998@mail.ru,
[2]Nikolaev Institute of Inorganic Chemistry, 630090, Russia, Novosibirsk, Akad. Lavrentiev Ave., 3,
[3]N. N. Vorozhtsov Novosibirsk Institute of Organic Chemistry, 630090, Russia, Novosibirsk, Akad. Lavrentiev Ave., 9

TEMPERATURE AND EXCITATION WAVELENGTH DEPENDENT EMISSION OF SILVER(I) COMPLEXES WITH AN AMINOPYRIMIDINE LIGAND*

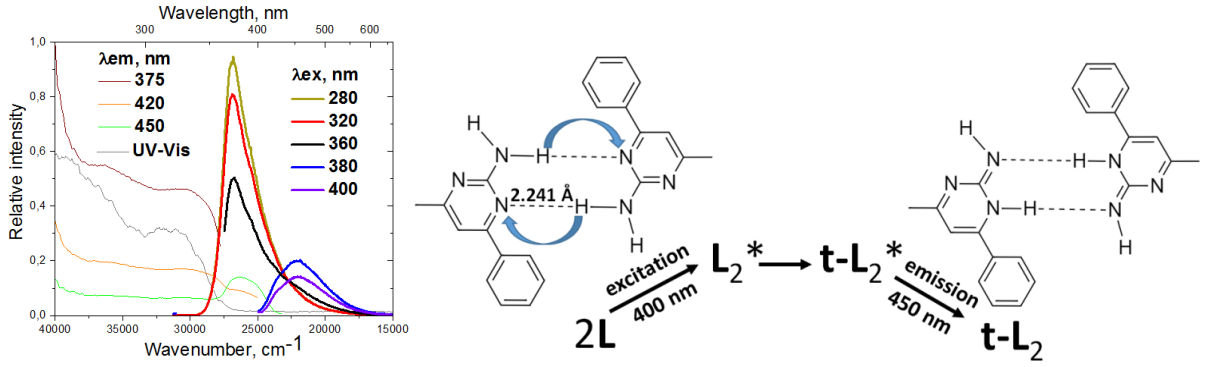
Keywords: photoluminescence, smart materials, pyrimidine, silver(I), TD-DFT calculations, excitation wavelength dependent emission.

Smart luminescent materials are compounds exhibiting tunable luminescence properties under various external stimuli. The design of smart materials has attracted growing interest because of their promising applications in sensors [1, 2], optoelectronic devices [3], biological labelling [4] and information encryption/anticounterfeiting [5, 6]. The aim of the work is to synthesize silver(I) complexes with 2-amino-4-phenyl-6-methylpyrimidine (L) and to study photoluminescence of the complexes at different excitation wavelengths and temperatures in the solid state.

The complex $[Ag_3L_2(NO_3)_3]_n$ (**1**) was synthesized by the reaction of $AgNO_3$ and L in a molar ratio 3:2 in $MeCN/CHCl_3$/EtOH (3:1:2). The complex **1** is a 3D coordination polymer. The X-ray crystal structure reveals three crystallographically independent Ag atoms. Molecules of L are ambidentately coordinated to Ag(I) ions by N^1 and N^3 atoms of the pyrimidine ring. The complex $[Ag_2L_2(PPh_3)_2(NO_3)_2]$ (**2**) was synthesized by the reaction of $AgNO_3$, L and PPh_3 in a molar ratio 1:1:1 in $MeCN/CHCl_3$ (1:2). The complex **2** is a dimeric complex; silver atoms are connected by two bridging NO_3^- anions. Photophysical properties of L and the complexes have been studied in the solid state at different temperatures. The emission spectrum of L depends on excitation energy (Fig. 1). The high-energy emission band at 375 nm

(τ = 0.6 ns) is caused by the fluorescence of the monomeric form of L**,** whereas low-energy emission band at 450 nm (τ = 2.4 ns) is attributed to an emission of a tautomeric structure t–L_2*. It seems that there is a double proton transfer from NH_2 groups to the aza-nitrogen atoms (fig. 1).

The complexes **1** and **2** demonstrate unique excitation wavelength dependent photoluminescence in the solid state caused by the presence of three emission mechanisms (fig. 2). The spectroscopic and computational results reveal that these emission mechanisms of the complexes can be assigned to ^{3}(M+X)LCT (X = NO_3^-) phosphorescence, excimer $^3\pi$-π* phosphorescence and ligand-centered $^1\pi$-π* fluorescence. The luminescence of the complex **1** at λ_{ex} = 340 nm shows a reversible thermochromic behavior. The emission color changes from blue-green at 77 K to yellowish green at 175 K and to white at 300 K.



Figere 1. Emission, excitation and diffuse reflectance spectra of L in the solid state at 300 K (left); an excited state double proton transfer of the compound L (right)

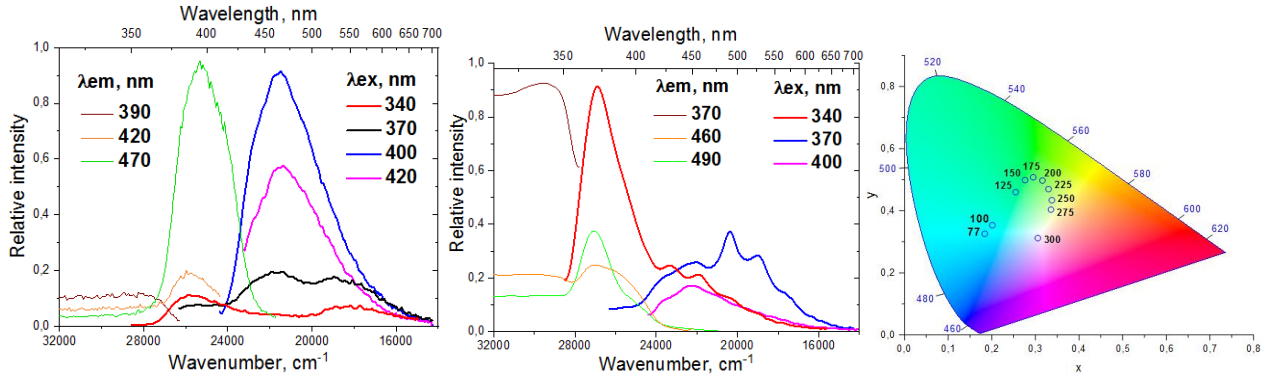


Figure 2. Emission and excitation spectra in the solid state at 300 K of **1** (left), of **2** (middle); CIE chromaticity diagram of **1** recorded at different temperatures (λ_{ex} = 340 nm, right)

References

1. *Gładysiak A., Nguyen T. N., Bounds R. et al.* // Chem. Sci. 2019. Vol. 10. P. 6140−6148.
2. *Li Y., Hu Y., Zhao Y. et al.* // Adv. Mater. 2011. Vol. 23. P. 776–780.
3. *Bai G., Tsang M.-K., Hao J.* // Adv. Funct. Mater. 2016. Vol. 26. P. 6330−6350.
4. *Wen T., Yang B., Guo Y. et al.* // Phys. Chem. Chem. Phys. 2014. Vol. 16. P. 23188–23195.
5. *Shi C., Shen X., Zhu Y. et al.* // ACS Appl. Mater. Interfaces. 2019. Vol. 11. P. 18548−18554.
6. *Kumar P., Singh S., Gupta B. K.* // Nanoscale. 2016. Vol. 8. P. 14297−14340.

** The research was supported by the President of the Russian Federation Grant for young scientists MK-1219.2020.3; by Russian Foundation for Basic Research and the government of the Novosibirsk region of the Russian Federation, grant № 18–43–540016 r_a.*

УДК 632.959

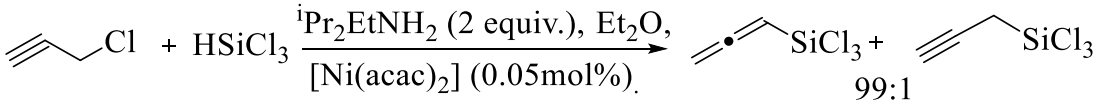
V. Y. Vaganov[1], Y. Fukazawa[2], S. A. Shipilovskikh[1], A. E. Rubtsov[1], A. V. Malkov[2]

[1]Perm State University,
614990, Russia, Perm, Bukireva St., 15,
vaganov@psu.ru,
[2]Loughborough University,
LE11 3TU, U. K., Loughborough,

ENANTIOSELECTIVE PROPARGYLATION OF ALDEHYDES CATALYZED BY NEW CHIRAL LEWIS BASES*

Keywords: Lewis base catalysis, enantioselective catalysis, allenyltrichlorosilane, homopropargylic alcohols.

Optically active homopropargylic alcohols are rare type of organic compounds due to the synthetic potential of acetylene group. They can be highly functional building blocks which found an application in the total synthesis of some biologically active compounds [1]. But the direct catalytic synthesis of this class of compounds appears to be challenging. Nowadays several methods of enantioselective propargylation have been developed. Some of these methods include using highly toxic reagents, such as tin compounds, some protocols requires an expensive reagents such as propargyl borolane. At this point using an allenylsilane as the propargylation agent is the most promising.



S. Kobayashi at.all. Tetrahedron, 2006. 62(2-3): p. 496-502.

However, the development of catalysts for asymmetric propargylations using allenyltrichlorosilanes has proved much more challenging [2]. To our knowledge there are only two examples of using this reagent in asymmetric catalysis [2, 3].